AD-A042 045   CALIFORNIA UNIV BERKELEY DEPT OF CHEMICAL ENGINEERING   F/G 7/4
               RHEOPTICAL STUDIES OF BLENDS OF POLY(STYRENE-B-BUTADIENE-B-STYR--ETC(U).
               JUL 77 S D HONG, M SHEN, T RUSSELL, R S STEIN   N00014-75-C-0955
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Technical Report No. 14

RHEOPTICAL STUDIES OF BLENDS OF POLY(STYRENE-

B-BUTADIENE-B-STYRENE) AND POLYSTYRENE.

by

S. D. Hong and M. Shen
Department of Chemical Engineering
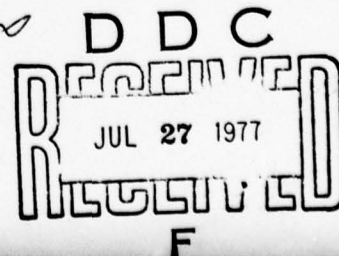University of California
Berkeley, California 94720

and

T. Russell and R. S. Stein
Department of Polymer Science of Engineering
and Polymer Research Institute
University of Massachusetts
Amherst, Massachusetts 01003

July 1, 1977

Technical Report to be published in
Proceedings of Symposium on Polymer Alloys

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REPORT DOCUMENTATION PAGE

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Rheoptical Studies of Blends of Poly-(Styrene-b-Butadiene-b-Styrene) and Polystyrene.	Technical Report
	6. PERFORMING ORG. REPORT NUMBER
	TR - 14

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
S. D. Hong, and M. Shen, T. Russell and R. S. Stein	N00014-75-C-0955

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Department of Chemical Engineering University of California Berkeley, California 94720	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research (Code 472) 800 N. Quincy Street Arlington, Virginia 22217	July 1, 1977
	13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
23p.	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Rheo-optical properties; Polyblends; Block Copolymers.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Polyblends of poly(styrene-b-butadiene) and polystyrene were cast from a tetrahydrofuran/methyl ethyl ketone mixture using a spin caster. These samples were found to undergo a "strain-induced plastic-rubber transition" upon deformation. Infrared dichroism, birefringence, small angle x-ray scattering, small angle light scattering and scanning electron micrograph studies

were carried out to investigate this phenomenon. Infrared dichroism and birefringence studies both indicate the high orientation of the polybutadiene chains, but not of the polystyrene chains, upon stretching. Thus most of the deformation after the "transition" has taken place is due to the rubbery domains. Small angle x-ray scattering results reveal that the morphology in the three coordinate directions was different. Upon stretching, the polystyrene domains may have broken up into smaller sub-domains which could be responsible for the observed plastic-rubber transition. The small angle light scattering and scanning electron micrograph results appear to be consistent with the above proposed interpretations.

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AND POLYSTYRENE.

S. D. Hong[*] and M. Shen

Department of Chemical Engineering
University of California
Berkeley, California 94720
            and
T. Russell and R. S. Stein
Department of Polymer Science of Engineering
    and Polymer Research Institute
University of Massachusetts
Amherst, Massachusetts 01003

ABSTRACT

Polyblends of poly(styrene-b-butadiene-b-styrene) and poly-
styrene were cast from tetrahydrofuran/methyl ethyl ketone mixture
using a spin caster. These samples were found to undergo "strain-
induced plastic-rubber transition" upon deformation. Infrared
dichroism and birefringence studies both indicate the high orienta-
tion of the polybutadiene chains, but not of the polystyrene chains.
Thus most of the deformation after the "transition" has taken place
is due to the rubbery domains. Scanning electron micrographs show
some surface fracture upon stretching for those samples containing
high polystyrene content. Small angle x-ray scattering results
reveal that the morphology in the three coordinate directions was
different. Upon stretching, the polystyrene domains may have
broken up into smaller sub-domains, which could be responsible for
the observed plastic-rubber transition. Furthermore, there was a
decrease in the total scattering intensity for the stretched sam-
ples, indicating a change in the mean square fluctuation of elec-
tron density of the stretched sample. The small angle light scat-
tering patterns appear to be consistent with the above proposed
interpretations.

*   Jet Propulsion Laboratory,   4800 Oak Grove Drive
    Pasadena, California 91103

INTRODUCTION

Polymer blends in general have synergetic properties which the individual homopolymers do not have. High impact polystyrene and ABS block copolymers are excellent examples. Because polymers are generally found to be incompatible as a consequence of positive free energy of mixing, most polymer blends exhibit phase separation (1-3). Blends of incompatible homopolymer do not have good mechanical properties because of the lack of sufficient adhesion between the different phases (4-6). An alternate process to improve adhesion between different phases in a blend is to add a graft copolymer or block copolymer. It was found that the use of these copolymers as additives in homopolymer blends greatly improve the mechanical properties of the blends (4-9). The morphology and mechanical properties of these blends have been studied by a number of workers (10-17).

Upon deformation block copolymers and blends of copolymer and homopolymer often exhibit stress softening (18-20). Furthermore the deformed samples demonstrate a healing effect in that, upon removal of stress, properties of the original undeformed sample are restored (18,20). For example, when a sample of the blend of poly(styrene-b-butadiene-b-styrene) and polystyrene is strained beyond the yield point, it becomes rubbery and exhibits high elasticity rather than irreversible drawing (20). The stress-softening effect in pure block copolymer has previously been attributed to the breaking up of some sort of rigid structures (18,21, 22) and the healing effect to the reformation of the original domain structures (18). Inoue et al., (15), on the other hand, found that in the blends of poly(styrene-b-isoprene) with polystyrene, the sample underwent yielding upon stretching. In this work, a rheo-optical investigation of the strain-induced plastic-rubber transition is presented in an effort to further elucidate the mechanism of this interesting phenomenon.

EXPERIMENTAL

Poly(styrene-b-butadiene-b-styrene) block copolymer (SBS), designated as Kraton 1101, was received from Shell Chemical Company. The copolymer contains 28% polystyrene and 72% polybutadiene. The weight average molecular weight of the copolymer is 84,000 and the polydispersity index is 1.21. The styrene blocks of the copolymer have a number average molecular weight of 13,300. The polybutadiene (PB) blocks have 46% trans-1,4, 46% cis-1,4 and 8% vinyl structures. Polystyrene (PS) was supplied by Polysciences, Inc., and has a number average molecular weight of 41,000 and polydispersity index of 2.32.

Samples of the block copolymer and its blends with PS were cast in the form of sheets from 10% solution of tetrahydrofuran

and methyl ethyl ketone mixture (90/10 in volume ratio). A spin caster was used for casting. The cast films were heated in vacuo at 60°C until constant weight was reached, indicating that the residual solvent had been removed.

Small angle x-ray scattering (SAXS) measurements were made with a Kratky small angle x-ray camera equipped with a Kratky-Siemans x-ray tube operated at 40 Kv and 20 mA. The intensity was measured with a proportional detector in conjunction with a pulse-height analyzer. Slit collimation was used and no desmearing corrections were made for the data presented. The resolution of the apparatus was set at 1800 Å . Small angle light scattering patterns were recorded on polaroid films using a He-Ne laser (Spectra-Physics) as light source. Scanning electron micrographs were obtained on an ETEC scanning electron microscope.

Infrared dichroism measurements were carried out using a Perkin-Elmer Model 180 Infrared Spectrophotometer equipped with a Perkin-Elmer silver bromide gold wire grid polarizer. A stretching device capable of extending both ends of the film simultaneously was used, thus the same part of the film remained in the beam at all elongations. Birefringence measurements were made with a Babinet compensator equipped with a mercury lamp as light source.

RESULTS AND DISCUSSION

Infrared Dichroism and Birefringence

The SBS and its blends with 10%, 20%, 30% and 40% PS all showed similar dichroic ratio vs. elongation relationships, therefore only the results for the SBS and its blend with 20% PS will be presented. The assignments of the absorption bands chosen for this study are summarized in Table I. Since almost all absorption bands associated with PS displayed negligible dichroism, only the results from two bands will be given.

The orientation of the transition moment with respect to the sample stretching direction may be given as (27):

$$f_M = \frac{D - 1}{D + 2} \tag{1}$$

where the dichroic ratio $D = A_{//}/A_{\perp}$; $A_{//}$ and $A_{\perp}$ are absorbance with the incident infrared beam polarized parallel and perpendicular to the stretching direction, respectively. f_M can be used to estimate the orientation of chain axis of the molecule provided the angle between the chain axis and the transition moment is known (27). In the present case, however, this information is not

Table 1. Assignments of IR Absorption Bands

Frequency (cm^{-1})	Assignment
1602, 1493	The C=C skeletal in-phase vibration of the aromatic ring in polystyrene (23,24)
1410	CH_2 in-phase deformation of $-CH=CH_2$(23) or CH in-plane bending of cis $-CH=CH-$ (25)
1310	CH bending of cis 1,4 polybutadiene (26)
1243	Associated with polybutadiene (25)

available. Thus we will use f_M as a qualitative indication of molecular orientation.

Figs. 1 and 2 show f_M as a function of elongation for the SBS and its blend with 20% PS. One may note that value for f_M for the absorption bands 1602 cm^{-1} and 1493 cm^{-1} (and other bands not shown) associated with vibration in PS chains are negligible. Although in this case the angle between the transition moment and the chain axis is close to 54.7°, the value of f_M is always very small even if the molecules have very high orientation (27). However, since in the present case the values of f_M for all the absorption bands associated with PS are very small, it may be reasonable to conclude that PS chains have negligible orientation. On the other hand, the absorption bands associated with the vibration of PB chains have noticeable orientation. The values of f_M for different absorption bands are different, because the angle between the transition moment and the chain axis for each chain may be different. Furthermore, it has been shown theoretically (28,29) and experimentally (30) that the orientations of chain segments in the amorphous regions are conformation-dependent. The chain segments of different conformations in the same parent chain may have different orientation.

Fig. 3 shows the birefringence of the SBS and the blend with 20% PS as a function of elongation. The samples have positive birefringences at all elongations. This is in contrast to the case of poly(styrene-b-isoprene) in which the birefringence measured in the necked regions was reported to be negative due to the orientation of PS (15).

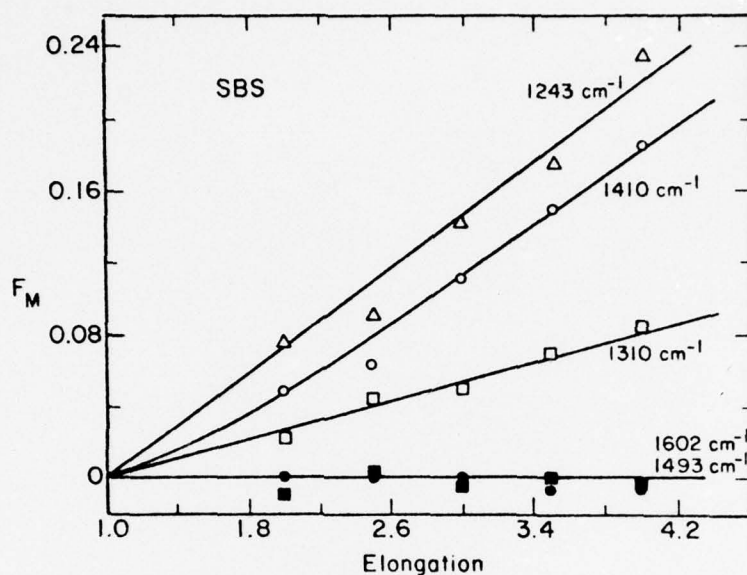The birefringence of a heterophase copolymer may be expressed in the form (31)

Figure 1. Orientation functions of transition moment of various infrared absorption hands of polybutadiene and polystyrene components in SBS.
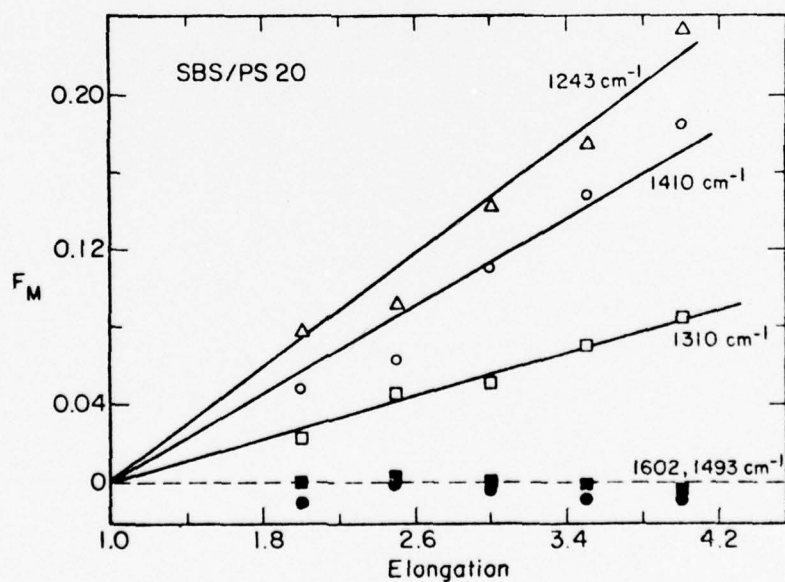

Figure 2. Orientation function of transition moment of various infrared absorption hands of polybutadine and polystyrene components in blend of SBS/20% PS
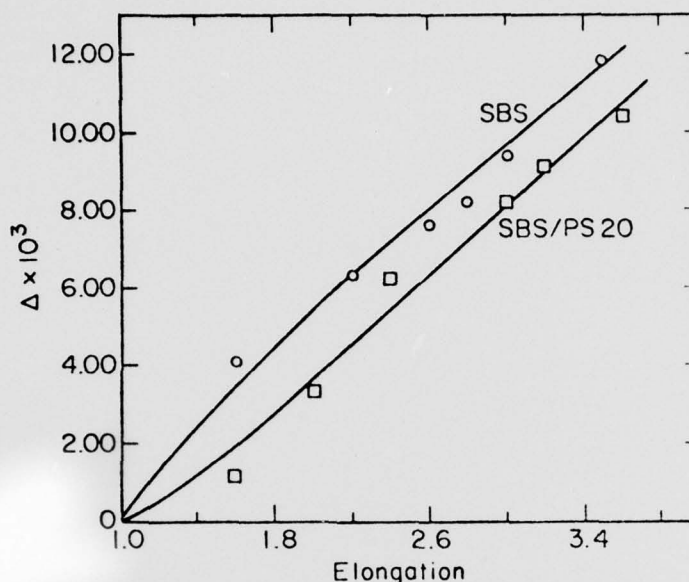
Figure 3. Birefringence vs. elongation for the
SBS (○) and SBS/20% PS (■)

$$\Delta = \phi_B C_B \sigma_B + \phi_S C_S \sigma_S + \Delta_f \tag{2}$$

where S and B designate PS phase and PB phase separately, and ϕ_S and ϕ_B are volume fraction, C_S and C_B are stress-optical coefficients and σ_B and σ_S are stresses. Δ_f is form birefringence. The value of form birefringence for a SBS block copolymer (20% styrene content) with the PS domains forming perfectly oriented rod structure was estimated to be on the order of 5×10^{-4} (32). In our case, the unstretched samples had negligible birefringence, indicating a negligible form birefringence. As the samples are stretched, the value of form birefringence may increase as a result of orientation of the optic axis of the domains. However, the value of the form birefringence is not expected to exceed 5×10^{-4} because the domains cannot achieve a high degree of orientation. It is more likely that Δ_f is very small in the stretched samples because electron micrographs did not show any appreciable orientation of the PS domains upon stretching (33). The value of C_S was estimated to be -5.2×10^3 Brewsters if PS is in the rubbery state and 10.2 Brewsters if it is in the glassy state (19), while C_B was estimated to be 3.1×10^3 Brewsters from the following equations (31)

$$C_B = X_c C_c + X_t C_t \tag{3}$$

where X_c and X_t are the mole fractions of the cis and trans isomers in PB and $C_c = 2700$ Brewsters and $C_t = 4100$ Brewsters (15) are the respective stress optical coefficients. The contribution from the vinyl component is neglected.

Since significantly high values of positive birefringence were observed for the SBS and its blends after yield point, it seems to indicate that no appreciable orientation of PS chains has occurred. Otherwise one may expect the birefringence to be negative, as in the case of poly(styrene-b-isoprene) (15), because of the high negative value of C_S and the high value of σ_S in comparison with those of C_B and σ_B. This evidence seems to support the conclusion derived from infrared dichroism data discussed earlier.

From previous electron micrograph studies of SBS and its blends (11), the unstretched samples had a morphology of interconnecting PS domains and PB domains. The fact that PB chains were oriented while PS chains showed no orientation after yield point indicates that the continuity of polystyrene domains was disrupted to give smaller PS domains imbedded in polybutadiene matrix. Thus the PB phase must bear the bulk of the strain, resulting in chain orientation.

Small Angle X-Ray Scattering (SAXS)

The geometry of the SAXS scan is shown in Fig. 4, where the direction 1 is normal to the film surface, the direction 2 is parallel to the spin direction and the direction 3 perpendicular to both 1 and 2. The scattering profiles of the blend with 20% PS are shown in Fig. 5a for the unstretched sample, and in Fig. 5b for the stretched sample. The scattering profiles of the pure SBS are similar except for the different peak positions.

As can be seen from Fig. 5a, the scattering patterns are not the same in different directions, indicating an anisotropic morphology. This anisotropy may be a result of the relatively rapid rate of evaporation of the solvent in spin casting. It has been reported that the rate of evaporation of the solvent will greatly affect the morphology of the sample (34).

The unstretched sample shows a rather sharp scattering peak with the incident beam along the direction 1 (Fig. 5a). The same is true for SBS. These results indicate that the domains have higher regularity in the direction normal to the sample surface. There is a very intense scattering at lower angles when the incident beam is along the 2 direction (curve 2 of Fig. 5a), which appears to arise from total reflection, as shown in Fig. 6 in which the scattering profiles are seen to be dependent on the tilt angle.
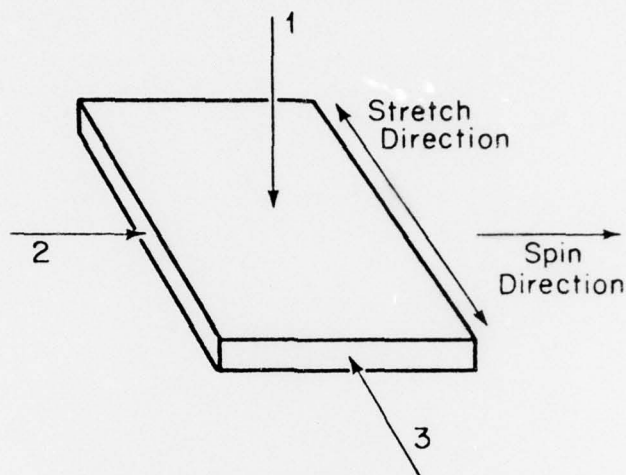
Figure 4. Geometry of SAXS scans. 1 is normal to the sample surface. 2 is the spin *direction of the spin caster* and 3 is the stretching direction.
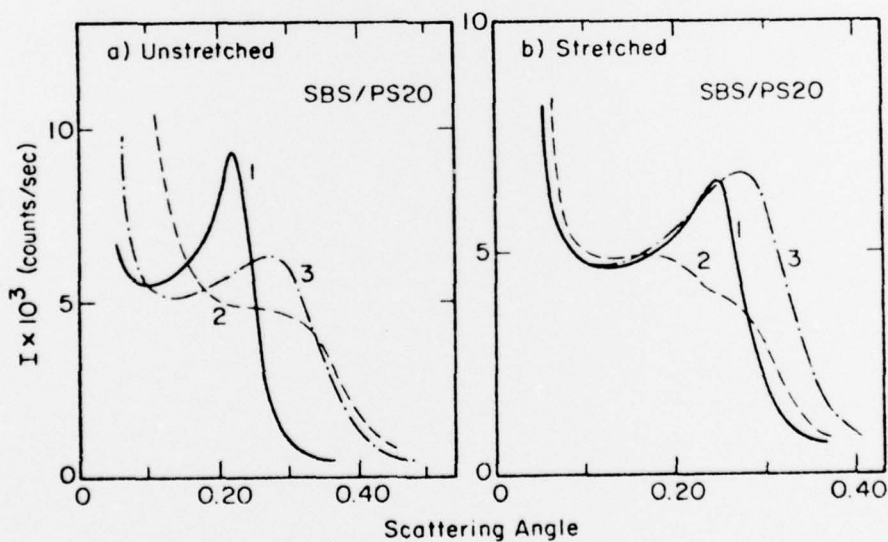

Figure 5. SAXS profiles for the blend of SBS/20% PS. (a) Sample unstretched. (b) Sample was stretched until the plastic-rubber transition completed. The stress was then released. The residual strain was less than 20%. Curves 1, 2 and 3 correspond to scanning geometry shown in Fig. 4.

The unstretched sample of the specimen in the beam also has weak second order scattering maxima in all three scattering profiles while the blend with 20% PS has second order scattering only when the incident beam is along the 1 direction.
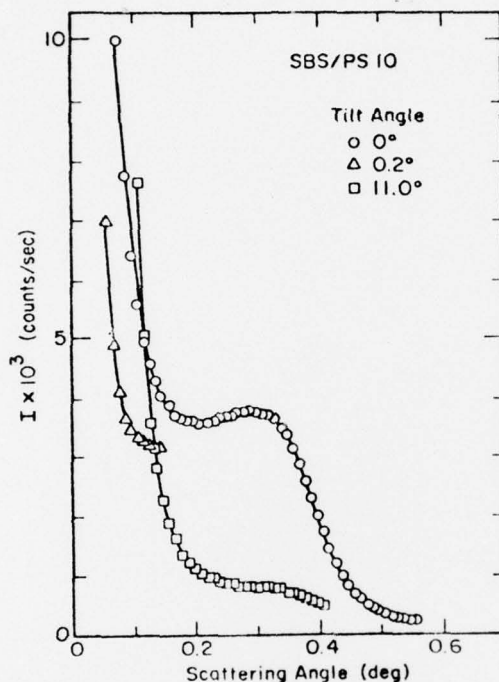

Figure 6. Scattering profiles of curve 2 in Fig. 5 with sample tilted at various angles.

Because the sample holder of the SAXS apparatus was not capable of holding an extended sample, the sample was first stretched until the plastic-rubber transformation was completed and then released. The residual strain was less than 20%. The scattering profiles show drastic changes, as shown in Fig. 5b. The scattering profiles become more diffuse and the first order scattering maxima are shifted to higher angles. However, the second order scattering maxima (not shown) are not present in the stretched sample.

While it may not be strictly valid, Bragg's law was used to estimate the change in interdomain spacings from the peak positions of the scattering curves. Since the residual strain remaining in the stretched sample was less than 20%, changes in the interdomain spacings from Bragg's law should serve as an approximate indication of morphological changes upon deformation. The results are summarized in Table 2.

Table 2. Positions of Observed Small-Angle Maxima ($\overset{\circ}{A}$)

Sample	Condition	Order of Maximum	Mode of View		
			1	2	3
SBS	Unstretched	1	366	306	309
		2	198	148	148
	Stretched	1	342	294	–
SBS/20% PS	Unstretched	1	443	355	355
		2	207	–	–
	Stretched	1	383	369	349
		2	177	–	–

There is a distinct decrease in the interdomain spacings with deformation as seen from the scattering curves for the case of the incident beam normal to the sample surface. The changes in the interdomain spacings when the incident beam is in the other two directions are not very certain because the scattering profiles are very diffuse. This decrease in interdomain spacings in conjunction with the more diffuse scattering profiles upon deformation seems to indicate that the polystyrene domains were disrupted into smaller domains. If the polystyrene domains maintained their integrity after deformation, one would not have expected such a pronounced change in interdomain spacings where less than 20% residual strain remained. This conclusion also agrees with a recent electron micrograph studies of a different SBS sample prepared under the same condition (33).

The effect of annealing the stretched sample at ambient temperature is shown in Fig. 7. Curve 1 is for the unstretched sample, curve 2 for the sample which was stretched and scanned immediately and curve 3 for the stretched sample which was kept (unstretched) at ambient temperature for 4 days. It is seen that upon annealing the scattering curve became more similar to that of the original sample, indicating a partial restoration of the original morphology. This reformation of the original morphology may correspond to the reported healing process observed in the mechanical properties of block copolymers and polyblends (10,18).

Small Angle Light Scattering (SALS)

The V_V (parallel polarized) and H_V (cross polarized) scattering patterns of SBS at various elongations are shown in Fig. 8. The
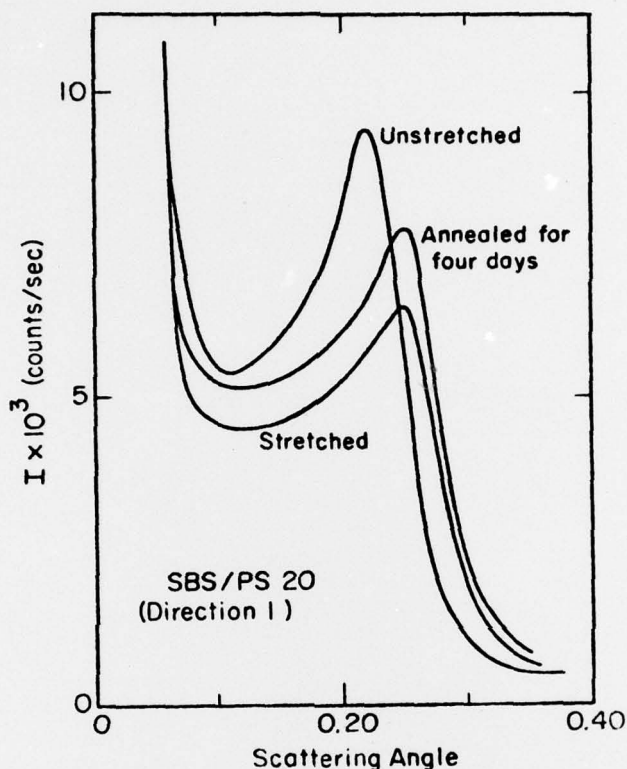
Figure 7.   Scattering profiles for a SBS/20% PS sample
            with different healing history. Curve 1,
            unstretched sample. Curve 2, scanned
            immediately after stretching. Curve 3, four
            days after stretching.

intensity of H_v scattering is very weak compared to the V_v
scattering. The exposure times for the H_v patterns were much
longer than those for the corresponding V_v scattering patterns.
In Fig. 9 the scattering of a blend of SBS with 10% PS in the
necked and unnecked regions of the sample after elongation.

    The unstretched samples of the pure blocks copolymer and its
blends have no detectable H_v scattering. The weak H_v scattering
of the stretched samples may be attributed to form birefringence
and orientational birefringence arising from the extension of
polymer chains, especially the PB chains. As discussed earlier,
the form birefringence of the unstretched samples is probably very
small but its magnitude will increase as the samples are extended.

    The fact that V_v scattering is much stronger than H_v scattering
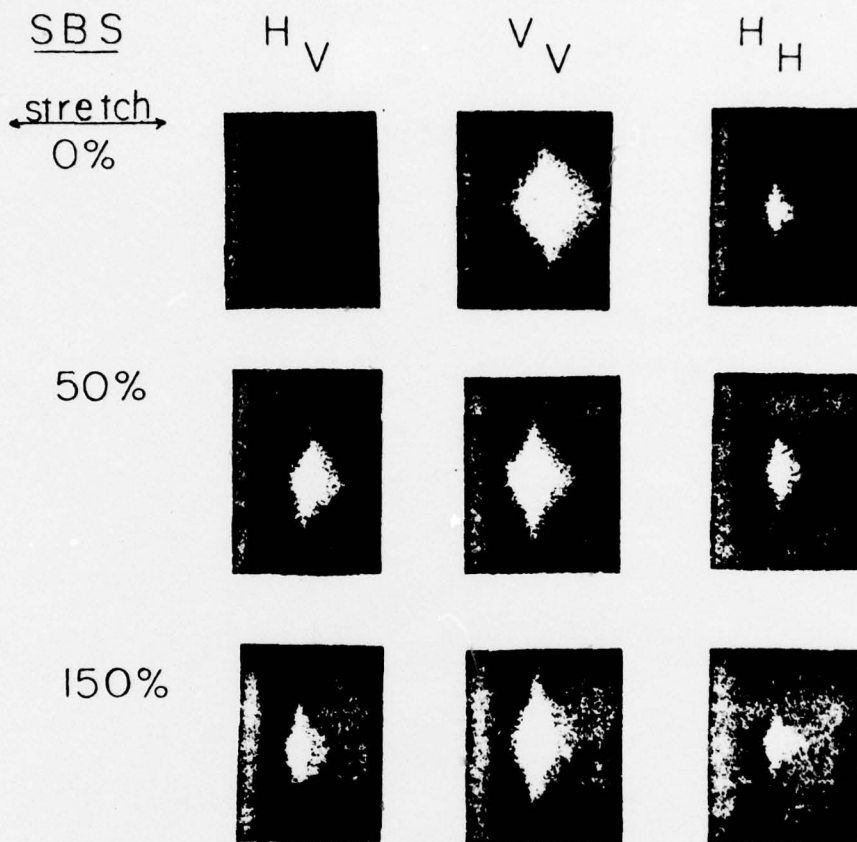suggests that correlated density fluctuation in the samples

Figure 8. V_V and H_V scattering patterns from film of SBS at various elongation.

dominate the scattering (36). For the unstretched samples, the V_V scattering pattern is almost circular for SBS, indicating a random correlation of the density fluctuation; whereas for the blends, the V_V scattering patterns are elliptical, indicating the existence of a regular domain arrangement in these samples (36,37). This is in agreement with the findings from previous work (11) in which the transmission electron micrographs showed no regularity of domain arrangement in SBS while in the blends there are regions of high regularity of domain arrangement.

Stretching gives characteristic changes of the V_V scattering patterns. The extent of changes increases with increasing amount of PS in the blend. The stretched sample of SBS, SBS/PS 10 and SBS/PS 20 have elliptical scattering patterns with different fine details. The major axis of the ellipsoid is perpendicular to the stretching direction. The stretched sample of SBS/PS 30 has a
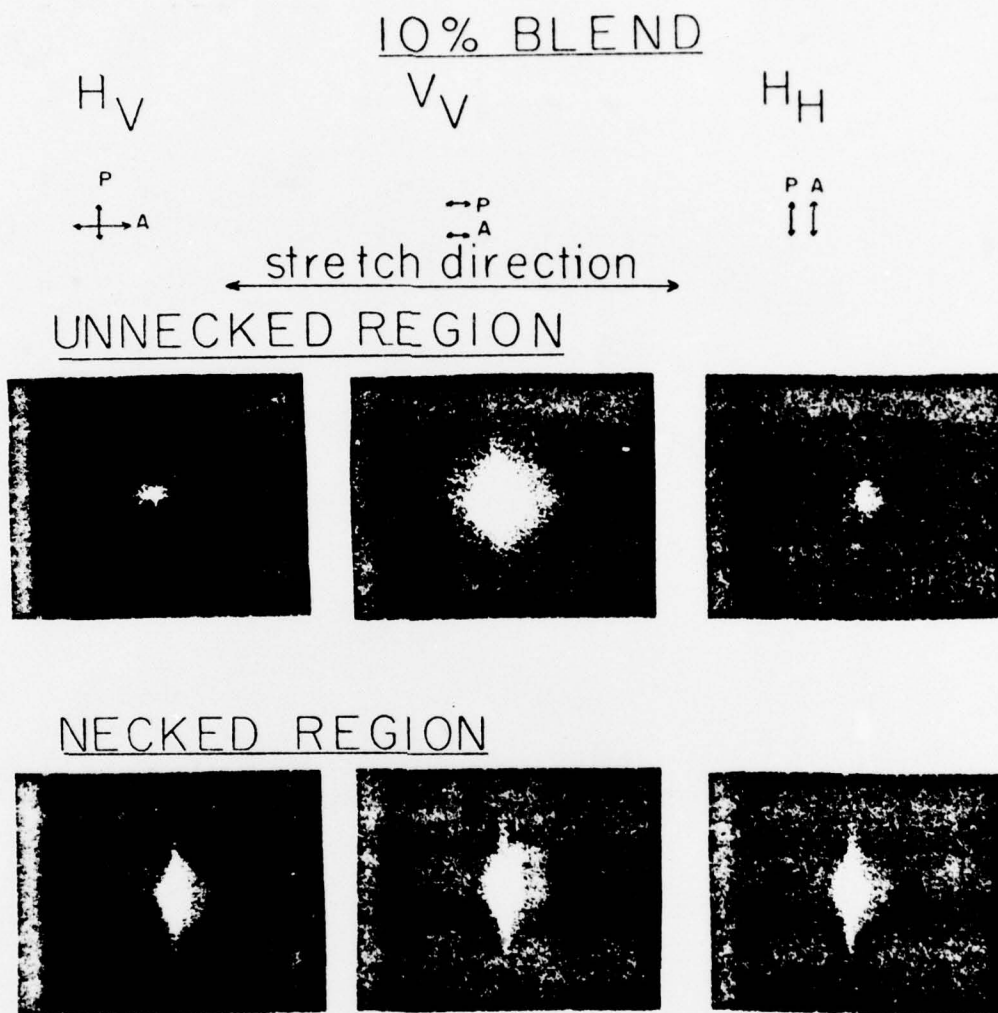
Figure 9. V_v scattering patterns from specimen films of SBS/PS 10, SBS/PS 20 and SBS/PS 30 at unstretched and stretched state.

dumbbell scattering patterns. All the new patterns remain in the same range of scattering angles as those for the unstretched sample, indicating that stretching does not change the range of correlation (36,37) at this elongation.

The characteristic changes of V_v scattering upon stretching may be attributed to changes in the correlation of density fluctuation (36,37) as a result of morphological changes and of another density fluctuation arising from newly formed heterogeneities due

to stretching (16). It has been observed that when an immersion
fluid was applied to the stretched samples, there was a decrease
in scattering intensity and, for SBS/PS 30, a slight change in
scattering pattern. Thus these newly formed heterogeneities must
be correlated to the voids or cracks developed in the styrene
domains upon stretching and are responsible for the plastic-rubber
transition.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the fractural surface of the
unstretched SBS and its blends with various amount of PS are
presented in Fig. 10, and the SEM of the stretched samples are
shown in Fig. 11. The samples were fractured at liquid nitrogen
temperature along the direction normal to the sample surface.

As shown in Fig. 10, the SBS does not show macroscopic phase
separation. On the other hand, macroscopic phase separation
occurs in all the blends forming a surface layer on the sample
surface and inclusions of polystyrene island in the bulk. The
macroscopic phase separation may arise because the added homo-
polystyrene has molecular weight higher than that of the corres-
ponding blocks in the block copolymer (35). The thickness of the
surface layer is not certain because there appears to be a tran-
sition between the surface layer and the bulk of the material,
especially for the 10% blend. The size of the PS islands seems to
increase with increasing homopolystyrene content. The actual
shapes of the islands are not certain. It was suggested from
studies of transmission electron micrographs of these sample (11)
that these islands were rod-like.

Upon deformation, as shown in Fig. 11, both the surface layer
and the inclusions underwent fracture. It is obvious that the
surface layer fractures are attributable to a continuous PS phase.
It is seen that in the polystyrene island fracture occurred across
the islands in the direction perpendicular to the strain rather
than on the boundaries. This seems to suggest that mixing of the
homopolystyrene and the polystyrene component in the block co-
polymer does occur in these islands, thus the adhesive force
between the block copolymer matrix and the islands is high enough
to strain the polystyrene islands beyond their fracture point.
It appears that fracture occurs mostly in the larger islands, per-
haps because they are more easily strained. On the other hand,
the smaller islands can simply move intact when the sample is
deformed. Another possibility is that the larger islands are more
likely to incorporate imperfections which are easily fractured.
The cracks appearing in the PS islands are not induced during
sample fracture in liquid nitrogen, since no cracks are observable
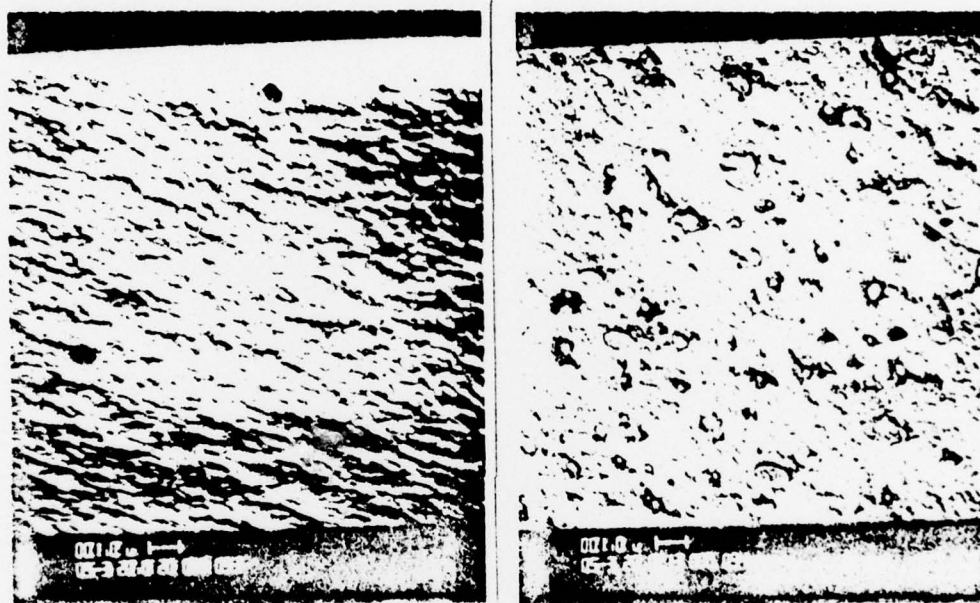on the fracture surface of the PS islands in the unstretched samples

Figure 10. Scanning electron micrographs of fracture surface of
SBS and 10% blend with PS. (The samples were
unstretched.) The fracture surfaces are parallel to
the normal to the sample surface. (a) The blends all
have a layer of PS on the sample surface, but the SBS
does not have it. (b) The blends have inclusion of
polystyrene islands in the bulk of the sample, the
SBS shows no inclusion. The sizes of the polystyrene
islands increase with increasing homopolystyrene
content.

Fig. 12 illustrates this point with the 30% blend.

Fig. 11 does not show any cracks formed in the regions outside
the PS islands. It is possible that the cracks formed in these
regions are too small to be resolved by the SEM. Since these
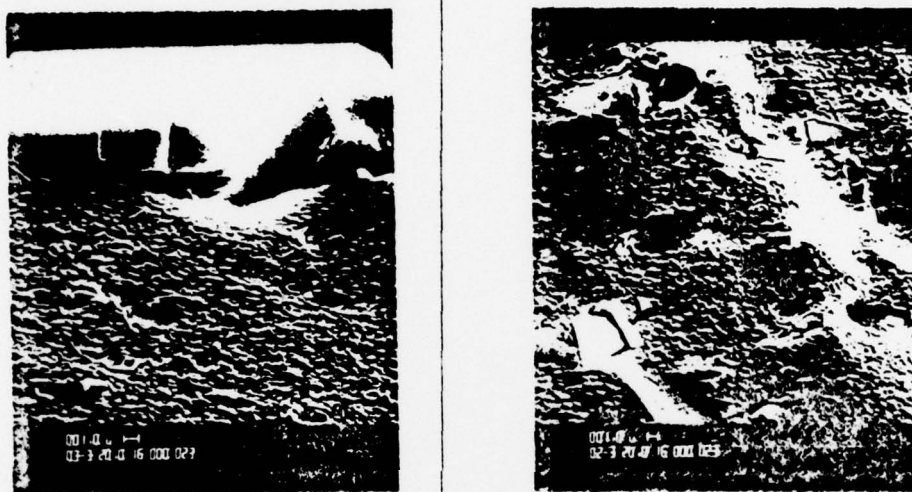islands are dispersed in the bulk of the material, the fracture of

Figure 11. Scanning electron micrographs of fracture surface of
the stretched samples of blends of SBS and PS
and the surface layer of a stretched SBS/30% PS sample.
Cracks are observed mainly in the larger PS
islands. (No cracks are seen in the regions outside
the PS islands.) Fractures occurred in the direction
perpendicular to the stretching.

these islands cannot account for the observed plastic-rubber
transformation. The fracture of the surface layer of the blends
may partially account for the yielding of these samples. However,
as shown by the previous transmission electron microscopy studies
(11), these samples have an interconnecting network of the PS as
well as PB domains. Thus the plastic-rubber transformation must
eventually involve the fracture of interconnected polystyrene
domains into the ones which are dispersed in the PB matrix, as
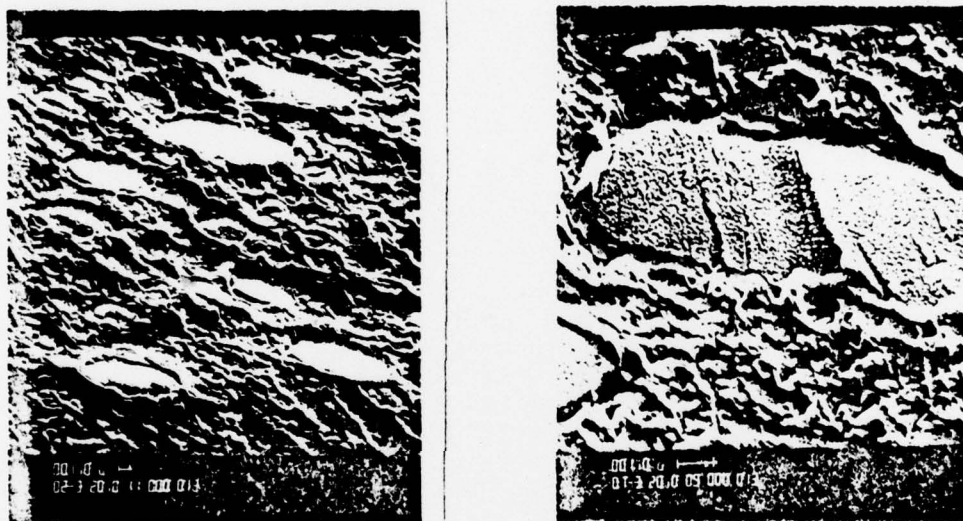manifested by the results presented previously.

Figure 12.   Fracture surface of an unstretched 30% blend indicating
the absence of cracks in the PS phase.

ACKNOWLEDGEMENT

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